

DESCRIPTION

CORROSION RESISTANT RARE EARTH MAGNETS AND  
PROCESS FOR PRODUCTION THEREOF

5

[0001]

TECHNICAL FIELD

This invention relates to corrosion resistant rare earth magnets in which rare earth magnets represented by R-T-M-B wherein R is at least one rare earth element inclusive of yttrium, T is iron or a mixture of iron and cobalt, and M is at least one element selected from among Ti, Nb, Al, V, Mn, Sn, Ca, Mg, Pb, Sb, Zn, Si, Zr, Cr, Ni, Cu, Ga, Mo, W, and Ta, and the contents of these elements are in the ranges: 5 wt% ≤ R ≤ 40 wt%, 50 wt% ≤ T ≤ 90 wt%, 0 wt% ≤ M ≤ 8 wt%, and 0.2 wt% ≤ B ≤ 8 wt%, are improved in corrosion resistance; and methods for preparing the same.

[0002]

BACKGROUND ART

Due to excellent magnetic properties, rare earth permanent magnets are on widespread use in a variety of applications including various electric appliances and computer peripheral devices. They are electrical and electronic materials of importance. In particular, Nd-Fe-B base permanent magnets are quite excellent permanent magnets, as compared with Sm-Co base permanent magnets, in that the predominant element Nd exists in more plenty than Sm, the expense of raw materials is low due to savings of cobalt, and their magnetic properties surpass those of Sm-Co base permanent magnets. In these years, the Nd-Fe-B base permanent magnets are used in increasing amounts and in more widespread applications.

[0003]

The Nd-Fe-B base permanent magnets, however, have the drawback that they are susceptible to oxidation in humid air within a brief time because they contain rare earth elements

and iron as predominant components. When they are incorporated in magnetic circuits, some problems arise that the output of magnetic circuits is reduced by such oxidation and the periphery is contaminated with rust.

5 [0004]

In particular, the Nd-Fe-B base permanent magnets have recently found use in motors such as automobile motors and elevator motors, where the magnets must work in a hot humid environment. It must be expected that the magnets are also 10 exposed to salt moisture during the service. It is thus required to endow the magnets with corrosion resistance at low costs. Additionally, in the manufacture process of such 15 motors, the magnets can be heated at or above 300°C, though briefly. In such a situation, the magnets must be heat resistant too.

[0005]

For improving the corrosion resistance of Nd-Fe-B base permanent magnets, various surface treatments like resin coating, aluminum ion plating and nickel plating are often 20 performed. With the state-of-the-art, however, it is difficult for such surface treatments to comply with the above-mentioned harsh conditions. For instance, resin coating is short of corrosion resistance and lacks heat 25 resistance. Nickel plating is prone to rust in salt moisture because of the presence of pinholes, though a few. Ion plating generally has good heat resistance and corrosion resistance, but is difficult to perform at low costs because of a need for large-scale apparatus.

[0006]

30 The references pertinent to the present invention include JP-A 2003-64454, JP-A 2003-158006, JP-A 2001-230107, and JP-A 2001-230108.

[0007]

#### DISCLOSURE OF THE INVENTION

35 Problem to Be Solved by the Invention

The present invention is made to provide R-T-M-B base rare earth permanent magnets such as Nd magnets which

withstand the use under the above-mentioned harsh conditions; and its object is to provide corrosion resistant rare earth magnets in which the magnets are provided with corrosion resistant, heat resistant coatings, and methods for preparing  
5 the same.

[0008]

Means for Solving the Problem

Making extensive investigations to attain the above object, the inventor has found that a rare earth permanent  
10 magnet represented by R-T-M-B wherein R is at least one element selected from rare earth elements including yttrium, T is iron or a mixture of iron and cobalt, and M is at least one element selected from the group consisting of Ti, Nb, Al, V, Mn, Sn, Ca, Mg, Pb, Sb, Zn, Si, Zr, Cr, Ni, Cu, Ga, Mo, W,  
15 and Ta, and the contents of these elements are in the ranges:  
5 wt% ≤ R ≤ 40 wt%, 50 wt% ≤ T ≤ 90 wt%, 0 wt% ≤ M ≤ 8 wt%,  
and 0.2 wt% ≤ B ≤ 8 wt%, can be converted into a rare earth magnet having corrosion resistance and heat resistance through the treatment of (i) applying a treating liquid  
20 comprising at least one flaky fine powder selected from the group consisting of Al, Mg, Ca, Zn, Si, Mn, and alloys thereof and at least one metal sol selected from the group consisting of Al, Zr, Si, and Ti to a surface of the magnet and then heating to form a composite film of flaky fine  
25 powder/metal oxide on the magnet surface; or (ii) applying a treating liquid comprising at least one flaky fine powder selected from the group consisting of Al, Mg, Ca, Zn, Si, Mn, and alloys thereof and a silane and/or a partial hydrolyzate thereof to a surface of the magnet to form a coating of flaky  
30 fine powder/silane and/or partially hydrolyzed silane and heating it to form a composite film on the magnet surface; or (iii) applying a treating liquid comprising at least one flaky fine powder selected from the group consisting of Al, Mg, Ca, Zn, Si, Mn, and alloys thereof and an alkali silicate  
35 to a surface of the magnet and then heating to form a composite film of flaky fine powder/alkali silicate glass on the magnet surface. In these ways, rare earth magnets having

corrosion resistance and heat resistance are obtainable. Determining several parameters on the basis of the above findings, the inventor has completed the present invention.  
[0009]

5       Accordingly, in a first aspect, the present invention provides a corrosion resistant rare earth magnet comprising a rare earth permanent magnet represented by R-T-M-B wherein R is at least one rare earth element including yttrium, T is iron or a mixture of iron and cobalt, and M is at least one 10 element selected from the group consisting of Ti, Nb, Al, V, Mn, Sn, Ca, Mg, Pb, Sb, Zn, Si, Zr, Cr, Ni, Cu, Ga, Mo, W, and Ta, and the contents of these elements are in the ranges:  
·    5 wt% ≤ R ≤ 40 wt%, 50 wt% ≤ T ≤ 90 wt%, 0 wt% ≤ M ≤ 8 wt%,  
·    and 0.2 wt% ≤ B ≤ 8 wt%, and a composite film of flaky fine  
15    powder/metal oxide formed on a surface of said magnet by  
·    treating the surface with a treating liquid comprising at  
    least one flaky fine powder selected from the group  
    consisting of Al, Mg, Ca, Zn, Si, Mn, and alloys thereof and  
    at least one metal sol selected from the group consisting of  
20    Al, Zr, Si, and Ti, followed by heating. As the means for  
    obtaining the corrosion resistant rare earth magnet of the  
    first aspect, the present invention also provides a method  
    for preparing a corrosion resistant rare earth magnet,  
    comprising the steps of applying a treating liquid comprising  
25    at least one flaky fine powder selected from the group  
    consisting of Al, Mg, Ca, Zn, Si, Mn, and alloys thereof and  
    at least one metal sol selected from the group consisting of  
    Al, Zr, Si, and Ti to a surface of a rare earth permanent  
    magnet, said rare earth permanent magnet being represented by  
30    R-T-M-B wherein R is at least one rare earth element  
    including yttrium, T is iron or a mixture of iron and cobalt,  
    and M is at least one element selected from the group  
    consisting of Ti, Nb, Al, V, Mn, Sn, Ca, Mg, Pb, Sb, Zn, Si,  
    Zr, Cr, Ni, Cu, Ga, Mo, W, and Ta, and the contents of these  
35    elements are in the ranges: 5 wt% ≤ R ≤ 40 wt%, 50 wt% ≤ T ≤  
    90 wt%, 0 wt% ≤ M ≤ 8 wt%, and 0.2 wt% ≤ B ≤ 8 wt%; and

heating to form a composite film of flaky fine powder/metal oxide on the magnet surface.

[0010]

In a second aspect, the present invention provides a  
5 corrosion resistant rare earth magnet comprising said rare  
earth permanent magnet and a composite film formed on a  
surface of said magnet by treating the surface with a  
treating liquid comprising at least one flaky fine powder  
selected from the group consisting of Al, Mg, Ca, Zn, Si, Mn,  
10 and alloys thereof and a silane and/or a partial hydrolyzate  
thereof, followed by heating. As the means for obtaining the  
corrosion resistant rare earth magnet of the second aspect,  
the present invention also provides a method for preparing a  
corrosion resistant rare earth magnet, comprising the steps  
15 of applying a treating liquid comprising at least one flaky  
fine powder selected from the group consisting of Al, Mg, Ca,  
Zn, Si, Mn, and alloys thereof and a silane and/or a partial  
hydrolyzate thereof to a surface of said rare earth permanent  
magnet to form a treatment coating of flaky fine  
20 powder/silane and/or partially hydrolyzed silane, and heating  
the treatment coating to form a composite film on the magnet  
surface. In one embodiment, the surface of the rare earth  
permanent magnet may be subjected to at least one  
pretreatment selected from pickling, alkaline cleaning and  
25 shot blasting, prior to the treatment with the treating  
liquid.

[0011]

In a third aspect, the present invention provides a  
corrosion resistant rare earth magnet comprising said rare  
30 earth permanent magnet and a composite film of flaky fine  
powder/alkali silicate glass formed on a surface of said  
magnet by treating the surface with a treating liquid  
comprising at least one flaky fine powder selected from the  
group consisting of Al, Mg, Ca, Zn, Si, Mn, and alloys  
35 thereof and an alkali silicate, followed by heating. As the  
means for obtaining the corrosion resistant rare earth magnet  
of the third aspect, the present invention also provides a

method for preparing a corrosion resistant rare earth magnet, comprising the steps of applying a treating liquid comprising at least one flaky fine powder selected from the group consisting of Al, Mg, Ca, Zn, Si, Mn, and alloys thereof and  
5 an alkali silicate to a surface of said rare earth permanent magnet, and heating to form a composite film of flaky fine powder/alkali silicate glass on the magnet surface.

[0012]

#### BENEFITS OF THE INVENTION

10 According to the invention, corrosion resistant rare earth magnets having heat resistance can be produced at low costs (i) by applying a treating liquid comprising at least one flaky fine powder selected from the group consisting of Al, Mg, Ca, Zn, Si, Mn, and alloys thereof and at least one  
15 metal sol selected from the group consisting of Al, Zr, Si, and Ti to a surface of the rare earth permanent magnet and then heating to provide a composite film of flaky fine powder/metal oxide to the magnet surface, or (ii) by applying a treating liquid comprising at least one flaky fine powder  
20 selected from the group consisting of Al, Mg, Ca, Zn, Si, Mn, and alloys thereof and a silane and/or a partial hydrolyzate thereof to a surface of the rare earth permanent magnet to form a coating of flaky fine powder/silane and/or partially hydrolyzed silane and heating it to provide a composite film  
25 to the magnet surface, or (iii) by applying a treating liquid comprising at least one flaky fine powder selected from the group consisting of Al, Mg, Ca, Zn, Si, Mn, and alloys thereof and an alkali silicate to a surface of the rare earth permanent magnet and then heating to provide a composite film  
30 of flaky fine powder/alkali silicate glass to the magnet surface. The invention is of great worth in the industry.

[0013]

#### BEST MODE FOR CARRYING OUT THE INVENTION

The rare earth permanent magnet used in the invention  
35 is a rare earth permanent magnet represented by R-T-M-B wherein R is at least one element selected from rare earth elements including yttrium, preferably neodymium or a

combination of predominant neodymium with another rare earth element(s), T is iron or a mixture of iron and cobalt, and M is at least one element selected from the group consisting of Ti, Nb, Al, V, Mn, Sn, Ca, Mg, Pb, Sb, Zn, Si, Zr, Cr, Ni, Cu, Ga, Mo, W, and Ta, and the contents of these elements are in the ranges: 5 wt% ≤ R ≤ 40 wt%, 50 wt% ≤ T ≤ 90 wt%, 0 wt% ≤ M ≤ 8 wt%, and 0.2 wt% ≤ B ≤ 8 wt%, typically a Nd-Fe-B permanent magnet.

[0014]

Herein, R is a rare earth element inclusive of yttrium, and specifically at least one element selected from among Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. It is preferred that R comprise Nd. The content of Nd is preferably in the range: 5 wt% ≤ Nd ≤ 37 wt%. The content of R is in the range: 5 wt% ≤ R ≤ 40 wt%, and preferably 10 wt% ≤ R ≤ 35 wt%.

[0015]

T is iron or a mixture of iron and cobalt. The content of T is in the range: 50 wt% ≤ T ≤ 90 wt%, and preferably 55 wt% ≤ T ≤ 80 wt%. It is preferred that the proportion of cobalt in T be equal to or less than 10% by weight.

[0016]

M is at least one element selected from the group consisting of Ti, Nb, Al, V, Mn, Sn, Ca, Mg, Pb, Sb, Zn, Si, Zr, Cr, Ni, Cu, Ga, Mo, W, and Ta. The content of M is in the range: 0 wt% ≤ M ≤ 8 wt%, and preferably 0 wt% ≤ M ≤ 5 wt%.

[0017]

Further, the magnet contains boron in an amount of 0.2 wt% ≤ B ≤ 8 wt%, and preferably 0.5 wt% ≤ B ≤ 5 wt%.

[0018]

The R-T-M-B permanent magnets such as Nd-Fe-B permanent magnets as used herein are prepared by first melting raw material metals in vacuum or an inert gas, preferably in an argon atmosphere. The raw material metals

used herein include pure rare earth elements, rare earth alloys, pure iron, ferroboron, and alloys thereof. It is understood that these metals contain incidental impurities which cannot be eliminated in the industrial manufacture,  
5 typically C, N, O, H, P and S. In the resulting alloy, alpha-Fe, R-rich phase or B-rich phase or the like can be left in addition to the  $R_2Fe_{14}B$  phase, and solution treatment may be optionally conducted. It may be a heat treatment in vacuum or an inert atmosphere like argon, at a temperature of  
10 700 to 1,200°C for at least one hour.

[0019]

The source metal thus prepared is then pulverized in stages of coarse grinding and fine milling into a fine powder. The average particle size may be in a range of 0.5  
15 to 20 µm. A size of less than 0.5 µm may be prone to oxidation, resulting in poor magnetic properties. A size of more than 20 µm may aggravate sinterability.

[0020]

The fine powder is then compacted into a predetermined  
20 shape using a press for compacting in a magnetic field, followed by sintering. Sintering is carried out at a temperature in the range of 900 to 1,200°C in vacuum or an inert atmosphere like argon, for at least 30 minutes. The sintering is followed by aging heat treatment at a lower  
25 temperature than the sintering temperature for at least 30 minutes.

[0021]

For the magnet manufacture, there may be employed not only the aforementioned method, but also the so-called  
30 two-alloy method of preparing high-performance Nd magnets by mixing alloy powders of two different compositions and sintering the mixture. Japanese Patent No. 2853838, Japanese Patent No. 2853839, JP-A 5-21218, JP-A 5-21219, JP-A 5-74618, and JP-A 5-182814 propose methods of preparing Nd magnets by  
35 determining the compositions of two types of alloy while taking into account the type and characteristics of magnet-constituting phases, and combining them, for thereby

producing high-performance Nd magnets having a good balance of high remanence (or residual magnetic flux density), high coercive force and high energy product. These manufacture methods may also be employed herein.

5 [0022]

The permanent magnet used herein contains incidental impurities which cannot be eliminated in the industrial manufacture, typically C, N, O, H, P and S, but desirably in a total amount of equal to or less than 2% by weight. More 10 than 2% by weight indicates the presence of more nonmagnetic components within the permanent magnet, which may detract from the remanence. Additionally, the rare earth elements 15 can be consumed by these impurities, leading to under-sintering and lower coercive forces. A smaller total amount of impurities is preferred because both remanence and coercive force become higher.

[0023]

According to the invention, any one of the following treatments (i), (ii), (iii) and combinations thereof is 20 carried out on a surface of the resulting permanent magnet to form a composite film thereon, obtaining a corrosion resistant rare earth magnet.

Treatment (i) of applying a treating liquid comprising a flaky fine powder and a metal sol to a surface of the 25 permanent magnet and then heating to form a composite film of flaky fine powder/metal oxide on the magnet surface.

Treatment (ii) of applying a treating liquid comprising a flaky fine powder and a silane and/or a partial hydrolyzate 30 thereof to a surface of the permanent magnet to form a coating of flaky fine powder/silane and/or partially hydrolyzed silane and heating it to form a composite film on the magnet surface.

Treatment (iii) of applying a treating liquid comprising a flaky fine powder and an alkali silicate to a surface of the 35 permanent magnet and then heating to form a composite film of flaky fine powder/alkali silicate glass on the magnet surface.

[0024]

These treatments are described below in detail.

First Treatment (i)

The first treatment uses a treating liquid comprising  
5 a flaky fine powder and a metal sol. The flaky fine powder  
used herein is of at least one metal selected from among Al,  
Mg, Ca, Zn, Si, and Mn, an alloy of two or more elements, and  
a mixture thereof. It is preferred to use a metal selected  
from among Al, Zn, Si, and Mn. The flaky fine powder used  
10 herein should preferably consist of particles of a shape  
having an average length of 0.1 to 15  $\mu\text{m}$ , an average  
thickness of 0.01 to 5  $\mu\text{m}$ , and an aspect ratio, given as  
average length/average thickness, of at least 2. More  
preferably, the flaky fine powder has an average length of 1  
15 to 10  $\mu\text{m}$ , an average thickness of 0.1 to 0.3  $\mu\text{m}$ , and an  
aspect ratio, given as average length/average thickness, of  
at least 10. With an average length of less than 0.1  $\mu\text{m}$ ,  
flaky particles may not lay in parallel to the underlying  
magnet, leading to a loss of binding force or adhesion. With  
20 an average length of more than 15  $\mu\text{m}$ , flakes can be lifted up  
by the solvent that evaporates from the treating liquid  
during heating process, so that flakes may not lay in  
parallel to the underlying magnet, resulting in a coating  
with poor binding force. Also for the dimensional accuracy  
25 of the coating, the average length is desirably equal to or  
less than 15  $\mu\text{m}$ . Flakes with an average thickness of less  
than 0.01  $\mu\text{m}$  can be oxidized on their surface in the flake  
preparing stage so that the coating may become brittle and  
less corrosion resistant. With an average thickness of more  
30 than 5  $\mu\text{m}$ , the dispersion of flakes in the treating liquid is  
aggravated so that flakes tend to settle down or the treating  
liquid may become unstable, resulting in poor corrosion  
resistance. With an aspect ratio of less than 2, flakes are  
unlikely to lay in parallel to the underlying magnet, leading  
35 to a loss of binding force. No upper limit is imposed on the

aspect ratio although an extremely high aspect ratio is undesired for economy. Most often, the upper limit of aspect ratio is 100. It is understood that the flaky fine powder used herein is commercially available. For example, Zn flakes are available under the trade name of Z1051 from Benda-Lutz, and Al flakes are available under the trade name of Alpaste 0100M from Toyo Aluminum Co., Ltd.

5 [0025]

As used herein, the average length and average thickness of flaky fine powder are determined by taking a photograph under an optical microscope or electron microscope, measuring the length and thickness of particles, and calculating an average thereof.

10 [0026]

15 The other component used herein is at least one metal sol selected from among Al, Zr, Si, and Ti. The metal sol may be prepared by hydrolyzing an alkoxide of at least one metal selected from among Al, Zr, Si, and Ti with water added or moisture to form a partially polymerized sol having a 20 binding ability.

[0027]

As just described, the metal sol used herein is one prepared by hydrolysis of a metal alkoxide. The metal alkoxide which can be used herein has the formula:

25



wherein A stands for Al, Zr, Si or Ti, "a" is the valence of the metal, and R stands for an alkyl group of 1 to 4 carbon atoms. The hydrolysis of such a metal alkoxide may be effected in an ordinary way.

30 [0028]

The metal alkoxide used herein is commercially available. To maintain the sol stable, a boron-containing compound such as boric acid or boric acid salt may be added to the sol in an amount of at most 10% by weight of the sol liquid. Sometimes, the boron-containing compound such as

boric acid or boric acid salt contributes to an improvement in corrosion resistance.

[0029]

The solvent for the treating liquid may be water or an  
5 organic solvent. The amounts of flaky fine powder and metal  
sol blended in the treating liquid are selected so as to  
provide the contents of flaky fine powder and metal oxide in  
the composite film to be described later.

[0030]

In preparing the treating liquid, various additives  
10 including dispersants, anti-settling agents, thickeners,  
anti-foaming agents, anti-skinning agents, desiccants, curing  
agents, anti-sagging agents, etc. may be added in amounts of  
at most 10% by weight for improving the performance thereof.  
15 Additionally, compounds such as zinc phosphates, zinc  
phosphites, calcium phosphites, aluminum phosphites, and  
aluminum phosphates may be added as corrosion-inhibiting  
pigments to the treating liquid in amounts of at most 20% by  
weight. These compounds capture metal ions which are  
20 dissolved out from the magnet and flaky fine powder, and form  
insolved complex, stabilizing the surface of Nd magnets or  
flaky metal fine particles through passivation.

[0031]

In the practice of the invention, the treating liquid  
25 is applied to the magnet by dipping or coating, after which  
heat treatment is effected for curing. The dipping and  
coating techniques are not particularly limited. Any  
well-known technique may be used to form a coating from the  
treating liquid. A heating temperature of from 100°C to less  
30 than 500°C is desirably maintained for at least 30 minutes in  
vacuum, air or inert gas atmosphere. Cure can take place  
even at temperatures below 100°C, but a long period of  
holding is necessary and undesirable from the standpoint of  
35 production efficiency. Under-cure may result in low binding  
forces and poor corrosion resistance. Temperatures equal to  
or higher than 500°C can damage the underlying magnet,  
causing to degrade magnetic properties. The upper limit of

heating time is not critical although it is generally about 1 hour.

[0032]

In forming the film, overcoating and heat treating  
5 steps may be repeated.

[0033]

Through the heating, the metal sol converts to a metal oxide past a gel state. As a consequence, the treatment coating becomes a composite film having a structure in which  
10 flaky fine particles are bound by the metal oxide. Although the reason why the composite film of flaky fine powder/metal oxide exhibits high corrosion resistance is not well understood, it is believed that fine particles in the form of flakes generally lay in parallel to the underlying magnet and  
15 fully cover the magnet, achieving a barrier effect. When a metal or alloy having a more negative potential than the permanent magnet is used as the flaky fine powder, a so-called sacrificial corrosion-preventing effect is exerted that the particles are preferentially oxidized to restrain  
20 the underlying magnet from oxidation. There is another advantage that the composite film formed is of inorganic nature and has high heat resistance.

[0034]

In the composite film thus formed, the flaky fine powder is preferably present in an amount of at least 40% by weight, more preferably at least 45% by weight, even more preferably at least 50% by weight, and most preferably at least 60% by weight. The upper limit of powder content is suitably selected although it is preferably up to 99.9% by  
25 weight, more preferably 99% by weight, and most preferably up to 95% by weight. Less than 40 wt% of the fine powder may be too small to fully cover the underlying magnet, leading to a decline of corrosion resistance.

[0035]

35 In the composite film thus formed, the metal oxide is preferably present in an amount of at least 0.1% by weight, more preferably at least 1% by weight, and most preferably at

least 5% by weight. The upper limit is preferably up to 60% by weight, more preferably up to 55% by weight, even most preferably up to 50% by weight, and most preferably up to 40% by weight. Less than 0.1 wt% of the metal oxide indicates a 5 too small amount of binding component, which may result in short binding forces. More than 60 wt% may detract from corrosion resistance.

[0036]

If the total of flaky fine powder and metal oxide does 10 not reach 100% by weight of the composite film, the remainder consists of the above-mentioned additives and/or corrosion-inhibiting pigments.

[0037]

It is desired that the film formed in the invention 15 have a thickness in the range of 1 to 40  $\mu\text{m}$ , preferably in the range of 5 to 25  $\mu\text{m}$ . Less than 1  $\mu\text{m}$  may lead to shortage of corrosion resistance whereas more than 40  $\mu\text{m}$  may lead to lower binding forces and become liable to delamination. A further increase of the film thickness may bring a 20 disadvantage to magnet use because the volume of R-Fe-B permanent magnet available for the same outline shape is reduced.

[0038]

#### Second Treatment (ii)

The second treatment uses a treating liquid comprising 25 a flaky fine powder and a silane and/or a partial hydrolyzate thereof. The flaky fine powder used herein is of at least one metal selected from among Al, Mg, Ca, Zn, Si, and Mn, an alloy of two or more elements, and a mixture thereof. 30 Otherwise, with respect to its shape (average length, average thickness, aspect ratio) and the like, the flaky fine powder is the same as that used in the first treatment (i).

[0039]

The other component is a silane which is preferably 35 selected from alkoxy silanes, more preferably trialkoxysilanes and dialkoxysilanes, and most preferably functional

group-containing organoalkoxysilanes or silane coupling agents of the general formula:



5

wherein "a" is 2 or 3;  $R^1$  is an alkyl group of 1 to 4 carbon atoms;  $R^2$  is selected from organic groups of 2 to 10 carbon atoms, including alkenyl groups such as vinyl and allyl, epoxy-containing alkyl groups, and (meth)acryloxy-containing alkyl groups; and  $R^3$  is selected from the same organic groups as defined for  $R^2$ , alkyl groups of 1 to 6 carbon atoms such as methyl, ethyl and propyl, and phenyl.

[0040]

Illustrative examples of the silane include  
15. vinyltrimethoxysilane, vinyltriethoxysilane,  
β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane,  
γ-glycidoxypropyltrimethoxysilane,  
γ-glycidoxypropylmethyldiethoxysilane,  
γ-glycidoxypropyltriethoxysilane,  
20 γ-methacryloxypropylmethyldimethoxysilane,  
γ-methacryloxypropyltrimethoxysilane,  
γ-methacryloxypropylmethyldiethoxysilane,  
γ-methacryloxypropyltriethoxysilane, alone or in admixture of  
two or more. The silanes which can be used herein are  
25 commercially available.

[0041]

The silane is partially hydrolyzed with water in the treating liquid or moisture whereby alkoxy groups are converted to silanol groups, exerting a binding ability. As 30 a proportion of silanol groups formed at this point becomes higher, the binding ability becomes better, but the treating liquid itself becomes less stable. It is described in JP-A 58-80245 and the like that when a boron-containing compound such as boric acid or a boric acid salt is added to a 35 treating liquid in an amount of at most 10% by weight, Si-O-B linkages are partially formed, contributing to the

stabilization of the treating liquid. Also in the present invention, a boron-containing compound such as boric acid or a boric acid salt may be used in the above-defined range. In some cases, the boron-containing compound such as boric acid 5 or a boric acid salt also contributes to an improvement in corrosion resistance.

[0042]

The solvent for the treating liquid may be water or an organic solvent. The amounts of flaky fine powder and silane 10 and/or partially hydrolyzed silane blended in the treating liquid are selected so as to provide the contents of flaky fine powder and condensate of silane and/or partially hydrolyzed silane in the composite film to be described later.

[0043]

In preparing the treating liquid, various additives including dispersants, anti-settling agents, thickeners, anti-foaming agents, anti-skimming agents, desiccants, curing agents, anti-sagging agents, etc. may be added in amounts of at most 10% by weight for performance-improving purposes like 15 improving the corrosion resistance of the film or improving the stability of the treating liquid. Additionally, compounds such as zinc phosphates, zinc phosphites, calcium phosphites, aluminum phosphites, and aluminum phosphates may be added as corrosion-inhibiting pigments to the treating 20 liquid in amounts of at most 20% by weight. These compounds capture metal ions which are dissolved out from the magnet and flaky fine powder, and form insolved complex, stabilizing the surface of Nd magnets or flaky metal fine particles 25 through passivation.

[0044]

In the practice of the invention, the treating liquid is applied to the magnet by dipping or coating, after which heat treatment is effected for curing. The dipping and coating techniques are not particularly limited. Any 35 well-known technique may be used to form a coating from the treating liquid. A heating temperature of from 100°C to less than 500°C is desirably maintained for at least 30 minutes in

vacuum, air or inert gas atmosphere. The heating temperature is more preferably from 200°C to 450°C and even more preferably from 250°C to 400°C. Cure can take place even at temperatures below 100°C, but a long period of holding is

5 necessary and undesirable from the standpoint of production efficiency. Under-cure may result in low binding forces and poor corrosion resistance. Temperatures equal to or higher than 500°C can damage the underlying magnet, causing to degrade magnetic properties. The upper limit of heating time  
10 is not critical although it is generally about 1 hour.

[0045]

In forming the film, overcoating and heat treating steps may be repeated.

[0046]

15 As a result of heating, the coating becomes a composite film having a structure in which flaky fine particles are reaction-bound by the condensate of silane and/or partially hydrolyzed silane. Although the reason why the composite film of flaky fine powder/silane and/or  
20 partially hydrolyzed silane exhibits high corrosion resistance is not well understood, it is believed that fine particles in the form of flakes generally lay in parallel to the underlying magnet and fully cover the magnet, achieving a barrier effect. When a metal or alloy having a more negative  
25 potential than the permanent magnet is used as the flaky fine powder, a so-called sacrificial corrosion-preventing effect is exerted that the particles are preferentially oxidized to restrain the underlying magnet from oxidation. There is another advantage that the composite film formed is of  
30 inorganic nature and has high heat resistance.

[0047]

In the composite film thus formed, the flaky fine powder is preferably present in an amount of at least 40% by weight, more preferably at least 45% by weight, even more preferably at least 50% by weight, and most preferably at least 60% by weight. The upper limit of powder content is suitably selected although it is preferably up to 99.9% by

weight, more preferably 99% by weight, and most preferably up to 95% by weight. Less than 40 wt% of the fine powder may be too small to fully cover the underlying magnet, leading to a decline of corrosion resistance.

5 [0048]

In the composite film thus formed, the condensate of silane and/or partially hydrolyzed silane is preferably present in an amount of at least 0.1% by weight, more preferably at least 1% by weight, and most preferably at 10 least 5% by weight. The upper limit is preferably up to 60% by weight, more preferably up to 55% by weight, even most preferably up to 50% by weight, and most preferably up to 40% by weight. Less than 0.1 wt% of the condensate indicates a 15 too small amount of binding component, which may result in short binding forces. More than 60 wt% may detract from corrosion resistance.

[0049]

If the total of flaky fine powder and condensate of silane and/or partially hydrolyzed silane does not reach 100% 20 by weight of the composite film, the remainder consists of the above-mentioned additives and/or corrosion-inhibiting pigments.

[0050]

It is desired that the composite film formed in the 25 invention have a thickness in the range of 1 to 40  $\mu\text{m}$ , preferably in the range of 5 to 25  $\mu\text{m}$ . Less than 1  $\mu\text{m}$  may lead to shortage of corrosion resistance whereas more than 40  $\mu\text{m}$  may lead to lower binding forces and become liable to delamination. A further increase of the film thickness may 30 bring a disadvantage to magnet use because the volume of R-Fe-B permanent magnet available for the same outline shape is reduced.

[0051]

Third Treatment (iii)

35 The third treatment uses a treating liquid comprising a flaky fine powder and an alkali silicate. The flaky fine

powder used herein is the same as that used in the first treatment (i).

[0052]

The other component is an alkali silicate which is 5 preferably at least one selected from lithium silicate, sodium silicate, potassium silicate, and ammonium silicate. These alkali silicates are commercially available.

[0053]

The solvent for the treating liquid may be water. The 10 amounts of flaky fine powder and alkali silicate blended in the treating liquid are selected so as to provide the contents of flaky fine powder and alkali silicate glass in the composite film to be described later.

[0054]

In preparing the treating liquid, various additives 15 including dispersants, anti-settling agents, thickeners, anti-foaming agents, anti-skinning agents, desiccants, curing agents, anti-sagging agents, etc. may be added in amounts of at most 10% by weight for improving the performance thereof. Additionally, compounds such as zinc phosphates, zinc 20 phosphites, calcium phosphites, aluminum phosphites, and aluminum phosphates may be added as corrosion-inhibiting pigments to the treating liquid in amounts of at most 20% by weight. These compounds capture metal ions which are dissolved out from the magnet and flaky fine powder, and form 25 insolved complex, stabilizing the surface of Nd magnets or flaky metal fine particles through passivation.

[0055]

In the practice of the invention, the treating liquid 30 is applied to the magnet by dipping or coating, after which heat treatment is effected for curing. The dipping and coating techniques are not particularly limited. Any well-known technique may be used to form a coating from the treating liquid. A heating temperature of from 100°C to less 35 than 500°C is desirably maintained for at least 30 minutes in vacuum, air or inert gas atmosphere. Cure can take place even at temperatures below 100°C, but a long period of holding is

necessary and undesirable from the standpoint of production efficiency. Under-cure may result in low binding forces and poor corrosion resistance. Temperatures equal to or higher than 500°C can damage the underlying magnet, causing to  
5 degrade magnetic properties. The upper limit of heating time is not critical although it is generally about 1 hour.

[0056]

In forming the film, overcoating and heat treating steps may be repeated.

10 [0057]

Through the heating, the alkali silicate converts to an alkali silicate glass. As a consequence, the treatment coating becomes a composite film having a structure in which flaky fine particles are bound by the alkali silicate glass.  
15 Although the reason why the composite film of flaky fine powder/alkali silicate glass exhibits high corrosion resistance is not well understood, it is believed that fine particles in the form of flakes generally lay in parallel to the underlying magnet and fully cover the magnet, achieving a  
20 barrier effect. When a metal or alloy having a more negative potential than the permanent magnet is used as the flaky fine powder, a so-called sacrificial corrosion-preventing effect is exerted that the particles are preferentially oxidized to restrain the underlying magnet from oxidation. There is  
25 another advantage that the composite film formed is of inorganic nature and has high heat resistance.

[0058]

In the composite film thus formed, the flaky fine powder is preferably present in an amount of at least 40% by  
30 weight, more preferably at least 45% by weight, even more preferably at least 50% by weight, and most preferably at least 60% by weight. The upper limit of powder content is suitably selected although it is preferably up to 99.9% by weight, more preferably 99% by weight, and most preferably up to 95% by weight. Less than 40 wt% of the fine powder may be too small to fully cover the underlying magnet, leading to a decline of corrosion resistance.

[0059]

In the composite film thus formed, the alkali silicate glass is preferably present in an amount of at least 0.1% by weight, more preferably at least 1% by weight, and most 5 preferably at least 5% by weight. The upper limit is preferably up to 60% by weight, more preferably up to 55% by weight, even most preferably up to 50% by weight, and most preferably up to 40% by weight. Less than 0.1 wt% of the alkali silicate glass indicates a too small amount of binding 10 component, which may result in short binding forces. More than 60 wt% may detract from corrosion resistance.

[0060]

If the total of flaky fine powder and alkali silicate glass does not reach 100% by weight of the composite film, 15 the remainder consists of the above-mentioned additives and/or corrosion-inhibiting pigments.

[0061]

It is desired that the film formed in the invention have a thickness in the range of 1 to 40  $\mu\text{m}$ , preferably in 20 the range of 5 to 25  $\mu\text{m}$ . Less than 1  $\mu\text{m}$  may lead to shortage of corrosion resistance whereas more than 40  $\mu\text{m}$  may lead to lower binding forces and become liable to delamination. A further increase of the film thickness may bring a disadvantage to magnet use because the volume of R-Fe-B 25 permanent magnet available for the same outline shape is reduced.

[0062]

It is understood that in the practice of the invention, pretreatment may be effected on the surface of the 30 magnet prior to the above treatment (i), (ii) or (iii). The pretreatment is at least one treatment selected from pickling, alkaline cleaning and shot blasting. Specifically effected is at least one pretreatment selected from (1) pickling + water washing + ultrasonic cleaning, (2) alkaline 35 cleaning + water washing, (3) shot blasting, and other treatments.

[0063]

The cleaning liquid used in pretreatment (1) is an aqueous solution containing at least one acid selected from among nitric acid, hydrochloric acid, acetic acid, citric acid, formic acid, sulfuric acid, hydrofluoric acid, permanganic acid, oxalic acid, hydroxyacetic acid, and phosphoric acid in a total amount of 1 to 20% by weight. The rare earth magnet may be dipped in the cleaning liquid which is kept at a temperature of normal temperature to 80°C. The pickling removes the oxide layer on the surface and helps improve the binding force of the composite film.

[0064]

The alkaline cleaning liquid which can be used in pretreatment (2) is an aqueous solution containing at least one member selected from among sodium hydroxide, sodium carbonate, sodium orthosilicate, sodium metasilicate, trisodium phosphate, sodium cyanide, and chelating agents in a total amount of 5 to 200 g/L. The rare earth magnet may be dipped in the cleaning liquid which is kept at a temperature of normal temperature to 90°C. The alkaline cleaning is effective for removing oil and fat contaminants which have attached to the magnet surface and helps improve the binding force between the composite film and the magnet.

[0065]

The blasting material used in pretreatment (3) may be ordinary ceramics, glass and plastics. Treatment may be conducted under a discharge pressure of 2 to 3 kgf/cm<sup>2</sup>. The shot blasting removes the oxide layer on the magnet surface in a dry way and also helps improve the binding force.

[0066]

#### EXAMPLE

Examples and Comparative Examples are given below for illustrating the invention although the invention is not limited thereto.

It is noted that the average length and average thickness of flaky fine powder were determined by taking a photograph under an optical microscope, measuring the length

and thickness of 20 particles, and calculating an average thereof.

The thickness of a composite film was determined by cutting a magnet sample having a film formed thereon,  
5 polishing the section, and observing the clean section under an optical microscope.

[0067]

Test piece

High-frequency melting in an argon atmosphere was  
10 followed by casting to form an ingot of the composition:  
32Nd-1.2B-59.8Fe-7Co in weight ratio. The ingot was coarsely ground on a jaw crusher and then finely milled on a jet mill using nitrogen gas, obtaining a fine powder having an average particle size of 3.5  $\mu\text{m}$ . The fine powder was then filled in  
15 a mold with a magnetic field of 10 kOe applied and compacted under a pressure of 1.0 t/cm<sup>2</sup>. It was then sintered in vacuum at 1,100°C for 2 hours and age-treated at 550°C for one hour, yielding a permanent magnet. From the permanent magnet, a magnet disc having a diameter of 21 mm and a  
20 thickness of 5 mm was cut out. This was followed by barrel polishing and ultrasonic water washing, obtaining a test piece.

[0068]

Examples 1 to 4

As the treating liquid for forming a film, a sol was prepared by dispersing aluminum flakes and zinc flakes in a hydrolytic solution of a metal alkoxide listed in Table 1.  
25 The hydrolytic solution of metal alkoxide (sol) had been prepared by stirring a mixture of 50 wt% metal alkoxide, 44 wt% ethanol and 5 wt% deionized water in the presence of 1 wt% of hydrochloric acid having a molar concentration of 1 as a catalyst. The treating liquid was adjusted at this point such that the composite film as cured might contain 8 wt% of  
30 aluminum flakes (average length 3  $\mu\text{m}$ , average thickness 0.2  $\mu\text{m}$ ) and 80 wt% of zinc flakes (average length 3  $\mu\text{m}$ , average thickness 0.2  $\mu\text{m}$ ). The treating liquid was sprayed to the

test piece through a spray gun so that the composite film might have a thickness of 10  $\mu\text{m}$ , and then heated in a hot air drying furnace at 300°C in air for 30 minutes, forming a film. The composite film as cured had the aluminum and zinc 5 contents described just above while the remainder was an oxide derived from the hydrolytic solution of metal alkoxide (sol) listed in Table 1.

[0069]

The thus prepared sample was subjected to performance 10 tests as described below. The results are shown in Table 1.

(1) Salt spray test

According to the neutral salt water spraying test of JIS Z-2371. While 5% edible salt in water was continuously sprayed at 35°C, the time passed until brown rust generated 15 was measured as an index for evaluation.

(2) Film appearance after 350°C/4 hr. heating

The film was heated at 350°C for 4 hours, after which any change in the outer appearance was visually examined.

[0070]

20

Table 1

	Type of metal alkoxide	Salt spray test (hr.)	Film appearance after 350°C/4 hr. heating
Example 1	aluminum isopropoxide	1,000	intact
Example 2	titanium isopropoxide	1,000	intact
Example 3	ethyl silicate	1,000	intact
Example 4	zirconium butoxide	1,000	intact

[0071]

Comparative Examples 1 to 4

For comparison purposes, samples were prepared by 25 forming films on the test pieces by aluminum ion plating, nickel plating and epoxy resin coating while controlling so as to give a film thickness of 10  $\mu\text{m}$ . A salt spray test was

conducted on these samples. Also, the film was heated at 350°C for 4 hours, after which any change in the outer appearance was visually examined. The results are shown in Table 2. It is seen that the permanent magnets of the invention have both corrosion resistance and heat resistance as compared with the otherwise surface treated permanent magnets.

[0072]

Table 2

	Surface treatment film	Salt spray test (hr.)	Film appearance after 350°C/4 hr. heating
Comparative Example 1	none	1	discolored overall
Comparative Example 2	Al ion plating	200	intact
Comparative Example 3	Ni plating	50	discolored, local cracks
Comparative Example 4	resin coating	100	carbonized, partial fusion

10

[0073]

Examples 5 to 9

Samples were prepared using the treating liquid in Example 3 while changing only the film thickness. A crosshatch adhesion test and a salt spray test were conducted on these samples. The results are shown in Table 3. Too thin a film may lack corrosion resistance whereas too thick a film may have poor adhesion.

[0074]

20 The crosshatch adhesion test is as follows.

(3) Crosshatch adhesion test

According to the crosshatch test of JIS K-5400. Adhesion was evaluated by incising a film in lattice by a cutter knife to define 100 square sections of 1 mm, forcefully attaching Cellophane adhesive tape thereto, strongly pulling the tape apart at an angle of 45°, and counting the number of remaining sections.

[0075]

Table 3

	Film thickness ( $\mu\text{m}$ )	Salt spray test (hr.)	Crosshatch adhesion test
Example 5	0.5	50	100/100
Example 6	1.0	500	100/100
Example 7	10	1,000	100/100
Example 8	40	2,000	100/100
Example 9	50	2,000	80/100

[0076]

5 Examples 10 to 12

Samples were prepared as in Example 2 except that the content of flaky fine powder in the composite film was changed. A salt spray test was conducted on these samples. The flaky fine powder contained in the treating liquid was a powder mixture of flaky aluminum powder and flaky zinc powder (both average length 3  $\mu\text{m}$ , average thickness 0.2  $\mu\text{m}$ ) in a weight ratio of 1:10. The weight percent of the powder mixture in the treating liquid was determined such that the content of flaky fine powder in the composite film might have the value shown in Table 4. It is noted that the remainder of the composite film other than the flaky fine powder was an oxide derived from the sol described in Example 2. The results of the salt spray test are shown in Table 4.

Adjustment was made so as to give a film thickness of 10  $\mu\text{m}$ . A film having a too low proportion of flaky fine powder may have poor corrosion resistance.

[0077]

Table 4

	Flaky fine powder content (wt%)	Salt spray test (hr.)
Example 10	25	50
Example 11	60	500
Example 12	90	1,000

[0078]

5 Examples 13 to 25

Samples were prepared as in Example 1 except that the shape of flaky fine powder was changed. A crosshatch adhesion test and a salt spray test were conducted on these samples. Adjustment was made so as to give a film thickness of 10 µm. The results are shown in Table 5. It is seen from Examples 13 to 17 that adhesion may become poor if the average length is too short or too long. It is also seen from Examples 18 to 22 that corrosion resistance may become poor if the average thickness is too small or too large. It is seen from Examples 23 to 25 that adhesion may become poor if the aspect ratio is too low.

[0079]

Table 5

	Average length ( $\mu\text{m}$ )	Average thickness ( $\mu\text{m}$ )	Aspect ratio (average length/thickness)	Salt spray test (hr.)	Crosshatch adhesion test
Example 13	0.05	0.01	5	1,000	80/100
Example 14	0.1	0.02	5	1,000	100/100
Example 15	2	0.2	10	1,000	100/100
Example 16	15	0.5	30	1,000	100/100
Example 17	20	0.5	40	1,000	80/100
Example 18	0.1	0.005	20	500	100/100
Example 19	0.1	0.01	10	1,000	100/100
Example 20	2	0.2	10	1,000	100/100
Example 21	15	5	3	1,000	100/100
Example 22	15	6	2.5	500	100/100
Example 23	0.75	0.5	1.5	1,000	80/100
Example 24	1.0	0.5	2	1,000	100/100
Example 25	10	0.5	20	1,000	100/100

[0080]

5 Examples 26 to 29

Samples were prepared by the same procedure as in Example 1 except that pretreatment as described below was conducted prior to the treatment with the treating liquid.

Pickling

10 composition: 10 vol% nitric acid + 5 vol% sulfuric acid  
dip at 50°C for 30 seconds

Alkaline cleaning

composition: 10 g/L sodium hydroxide,  
3 g/L sodium metasilicate, 10 g/L trisodium phosphate,  
15 8 g/L sodium carbonate, 2 g/L surfactant  
dip at 40°C for 2 minutes

Shot blasting

Aluminum oxide #220 was blasted under a discharge pressure of 2 kgf/cm<sup>2</sup>.

[0081]

5       The magnet having the film formed thereon was subjected to a pressure cooker test (PCT) at 120°C, 2 atmospheres, 200 hours, after which a crosshatch adhesion test was conducted. The results are shown in Table 6. It is evident that the binding force is improved by the  
10 pretreatment.

[0082]

Table 6

	Pretreatment	Crosshatch adhesion test after PCT
Example 26	none	90/100
Example 27	pickling + water washing + ultrasonic cleaning	100/100
Example 28	alkaline cleaning + water washing	100/100
Example 29	shot blasting	100/100

[0083]

15       Examples 30 to 39

As the treating liquid for forming a film, a dispersion was prepared by dispersing aluminum flakes and zinc flakes in water together with a silane listed in Table 7. The treating liquid was adjusted at this point such that the composite film  
20      as cured might contain 8 wt% of aluminum flakes (average length 3 µm, average thickness 0.2 µm) and 80 wt% of zinc flakes (average length 3 µm, average thickness 0.2 µm). The treating liquid was sprayed to the test piece through a spray gun so that the composite film might have a thickness of 10  
25      µm, and then heated in a hot air drying furnace at 300°C in air for 30 minutes, forming a film. The composite film as cured had the aluminum and zinc contents described just above

while the remainder was a condensate of the silane and/or partially hydrolyzed silane listed in Table 7.

[0084]

The thus prepared samples were subjected to the same 5 performance tests as in Examples 1 to 4 [(1) salt spray test and (2) film appearance after 350°C/4 hr. heating]. The results are shown in Table 7.

[0085]

Table 7

	Type of silane	Salt spray test (hr.)	Film appearance after 350°C/4 hr. heating
Example 30	vinyltrimethoxysilane	1,000	intact
Example 31	vinyltriethoxysilane	1,000	intact
Example 32	β-(3,4-epoxycyclohexyl)ethyl-trimethoxysilane	1,000	intact
Example 33	γ-glycidoxypropyltrimethoxysilane	1,000	intact
Example 34	γ-glycidoxypropylmethyl-diethoxysilane	1,000	intact
Example 35	γ-glycidoxypropyltriethoxysilane	1,000	intact
Example 36	γ-methacryloxypropylmethyl-dimethoxysilane	1,000	intact
Example 37	γ-methacryloxypropyltrimethoxysilane	1,000	intact
Example 38	γ-methacryloxypropylmethyl-diethoxysilane	1,000	intact
Example 39	γ-methacryloxypropyltriethoxysilane	1,000	intact

10

[0086]

Examples 40 to 44

Samples were prepared using the treating liquid in Example 32 while changing only the film thickness. As in 15 Examples 5 to 9, a crosshatch adhesion test and a salt spray test were conducted on these samples. The results are shown

in Table 8. Too thin a film may lack corrosion resistance whereas too thick a film may have poor adhesion.

[0087]

Table 8

	Film thickness ( $\mu\text{m}$ )	Salt spray test (hr.)	Crosshatch adhesion test
Example 40	0.5	50	100/100
Example 41	1.0	500	100/100
Example 42	10	1,000	100/100
Example 43	40	2,000	100/100
Example 44	50	2,000	80/100

[0088]

Examples 45 to 47

Samples were prepared as in Example 32 except that the content of flaky fine powder in the composite film was changed. A salt spray test was conducted on these samples. The flaky fine powder contained in the treating liquid was a powder mixture of flaky aluminum powder and flaky zinc powder (both average length 3  $\mu\text{m}$ , average thickness 0.2  $\mu\text{m}$ ) in a weight ratio of 1:10. The weight percent of the powder mixture in the treating liquid was determined such that the content of flaky fine powder in the composite film might have the value shown in Table 9. It is noted that the remainder of the composite film other than the flaky fine powder was a condensate of silane and/or partially hydrolyzed silane derived from the silane described in Example 32. The results of the salt spray test are shown in Table 9. Adjustment was made so as to give a film thickness of 10  $\mu\text{m}$ . A film having a too low proportion of flaky fine powder may have poor corrosion resistance.

[0089]

Table 9

	Flaky fine powder content (wt%)	Salt spray test (hr.)
Example 45	25	50
Example 46	60	500
Example 47	90	1,000

[0090]

5    Examples 48 to 60

·       Samples were prepared as in Example 30 except that the  
·       shape of flaky fine powder was changed. A crosshatch  
·       adhesion test and a salt spray test were conducted on these  
·       samples. Adjustment was made so as to give a film thickness  
10      of 10  $\mu\text{m}$ . The results are shown in Table 10. It is seen  
·       from Examples 48 to 52 that adhesion may become poor if the  
·       average length is too short or too long. It is also seen  
·       from Examples 53 to 57 that corrosion resistance may become  
·       poor if the average thickness is too small or too large. It  
15      is seen from Examples 58 to 60 that adhesion may become poor  
·       if the aspect ratio is too low.

[0091]

Table 10

	Average length ( $\mu\text{m}$ )	Average thickness ( $\mu\text{m}$ )	Aspect ratio (average length/thickness)	Salt spray test (hr.)	Crosshatch adhesion test
Example 48	0.05	0.01	5	1,000	80/100
Example 49	0.1	0.02	5	1,000	100/100
Example 50	2	0.2	10	1,000	100/100
Example 51	15	0.5	30	1,000	100/100
Example 52	20	0.5	40	1,000	80/100
Example 53	0.1	0.005	20	500	100/100
Example 54	0.1	0.01	10	1,000	100/100
Example 55	2	0.2	10	1,000	100/100
Example 56	15	5	3	1,000	100/100
Example 57	15	6	2.5	500	100/100
Example 58	0.75	0.5	1.5	1,000	80/100
Example 59	1.0	0.5	2	1,000	100/100
Example 60	10	0.5	20	1,000	100/100

[0092]

5    Examples 61 to 64

Samples were prepared by the same procedure as in Example 30 except that pretreatment as described below was conducted prior to the treatment with the treating liquid.

Pickling

10      composition: 10 vol% nitric acid + 5 vol% sulfuric acid  
             dip at 50° for 30 seconds

Alkaline cleaning

composition: 10 g/L sodium hydroxide,  
3 g/L sodium metasilicate, 10 g/L trisodium phosphate,  
15      8 g/L sodium carbonate, 2 g/L surfactant  
             dip at 40°C for 2 minutes

Shot blasting

Aluminum oxide #220 was blasted under a discharge pressure of 2 kgf/cm<sup>2</sup>.

[0093]

5       The magnet having the film formed thereon was subjected to a pressure cooker test (PCT) at 120°C, 2 atmospheres, 200 hours, after which a crosshatch adhesion test was conducted. The results are shown in Table 11. It is evident that the binding force is improved by the  
10 pretreatment.

[0094]

Table 11

	Pretreatment	Crosshatch adhesion test after PCT
Example 61	none	90/100
Example 62	pickling + water washing + ultrasonic cleaning	100/100
Example 63	alkaline cleaning + water washing	100/100
Example 64	shot blasting	100/100

[0095]

15   Examples 65 to 68

As the treating liquid for forming a film, a dispersion was prepared by dispersing aluminum flakes and zinc flakes in an alkali silicate listed in Table 12. The treating liquid was adjusted at this point such that the  
20 composite film as cured might contain 8 wt% of aluminum flakes (average length 3 µm, average thickness 0.2 µm) and 80 wt% of zinc flakes (average length 3 µm, average thickness 0.2 µm). The treating liquid was sprayed to the test piece through a spray gun so that the composite film might have a  
25 thickness of 10 µm, and then heated in a hot air drying furnace at 300°C in air for 30 minutes, forming a film. The composite film as cured had the aluminum and zinc contents

described just above while the remainder was an alkali silicate glass derived from the alkali silicate listed in Table 12.

[0096]

5 The thus prepared samples were subjected to the same performance tests as in Examples 1 to 4 [(1) salt spray test and (2) film appearance after 350°C/4 hr. heating]. The results are shown in Table 12.

[0097]

10

Table 12

	Type of alkali silicate	Salt spray test (hr.)	Film appearance after 350°C/4 hr. heating
Example 65	lithium silicate	1,000	intact
Example 66	potassium silicate	1,000	intact
Example 67	sodium silicate	1,000	intact
Example 68	ammonium silicate	1,000	intact

[0098]

Examples 69 to 73

15 Samples were prepared using the treating liquid in Example 65 while changing only the film thickness. As in Examples 5 to 9, a crosshatch adhesion test and a salt spray test were conducted on these samples. The results are shown in Table 13. Too thin a film may lack corrosion resistance whereas too thick a film may have poor adhesion.

[0099]

Table 13

	Film thickness ( $\mu\text{m}$ )	Salt spray test (hr.)	Crosshatch adhesion test
Example 69	0.5	50	100/100
Example 70	1.0	500	100/100
Example 71	10	1,000	100/100
Example 72	40	2,000	100/100
Example 73	50	2,000	80/100

[0100]

5 Examples 74 to 76

Samples were prepared as in Example 65 except that the content of flaky fine powder in the composite film was changed. A salt spray test was conducted on these samples. The flaky fine powder contained in the treating liquid was a powder mixture of flaky aluminum powder and flaky zinc powder (both average length 3  $\mu\text{m}$ , average thickness 0.2  $\mu\text{m}$ ) in a weight ratio of 1:10. The weight percent of the powder mixture in the treating liquid was determined such that the content of flaky fine powder in the composite film might have the value shown in Table 14. It is noted that the remainder of the composite film other than the flaky fine powder was an alkali silicate glass derived from the alkali silicate described in Example 65. The results of the salt spray test are shown in Table 14. Adjustment was made so as to give a film thickness of 10  $\mu\text{m}$ . A film having a too low proportion of flaky fine powder may have poor corrosion resistance.

[0101]

Table 14

	Flaky fine powder content (wt%)	Salt spray test (hr.)
Example 74	25	50
Example 75	60	500
Example 76	90	1,000

[0102]

5   Examples 77 to 89

Samples were prepared as in Example 65 except that the shape of flaky fine powder was changed. A crosshatch adhesion test and a salt spray test were conducted on these samples. Adjustment was made so as to give a film thickness of 10  $\mu\text{m}$ . The results are shown in Table 15. It is seen from Examples 77 to 81 that adhesion may become poor if the average length is too short or too long. It is also seen from Examples 82 to 86 that corrosion resistance may become poor if the average thickness is too small or too large. It is seen from Examples 87 to 89 that adhesion may become poor if the aspect ratio is too low.

[0103]

Table 15

	Average length ( $\mu\text{m}$ )	Average thickness ( $\mu\text{m}$ )	Aspect ratio (average length/thickness)	Salt spray test (hr.)	Crosshatch adhesion test
Example 77	0.05	0.01	5	1,000	80/100
Example 78	0.1	0.02	5	1,000	100/100
Example 79	2	0.2	10	1,000	100/100
Example 80	15	0.5	30	1,000	100/100
Example 81	20	0.5	40	1,000	80/100
Example 82	0.1	0.005	20	500	100/100
Example 83	0.1	0.01	10	1,000	100/100
Example 84	2	0.2	10	1,000	100/100
Example 85	15	5	3	1,000	100/100
Example 86	15	6	2.5	500	100/100
Example 87	0.75	0.5	1.5	1,000	80/100
Example 88	1.0	0.5	2	1,000	100/100
Example 89	10	0.5	20	1,000	100/100

[0104]

5 Examples 90 to 93

Samples were prepared by the same procedure as in Example 65 except that pretreatment as described below was conducted prior to the treatment with the treating liquid.

[0105]

10 Pickling

composition: 10 vol% nitric acid + 5 vol% sulfuric acid  
dip at 50°C for 30 seconds

[0106]

Alkaline cleaning

15 composition: 10 g/L sodium hydroxide,  
3 g/L sodium metasilicate, 10 g/L trisodium phosphate,  
8 g/L sodium carbonate, 2 g/L surfactant  
dip at 40°C for 2 minutes

[0107]

Shot blasting

Aluminum oxide #220 was blasted under a discharge pressure of 2 kgf/cm<sup>2</sup>.

5 [0108]

The magnet having the film formed thereon was subjected to a pressure cooker test (PCT) at 120°C, 2 atmospheres, 200 hours, after which a crosshatch adhesion test was conducted. The results are shown in Table 16. It  
10 is evident that the binding force is improved by the pretreatment.

[0109]

Table 16

	Pretreatment	Crosshatch adhesion test after PCT
Example 90	none	90/100
Example 91	pickling + water washing + ultrasonic cleaning	100/100
Example 92	alkaline cleaning + water washing	100/100
Example 93	shot blasting	100/100